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MASTER

EVALUATION OF HAZARDOUS-WASTE INCINERATION IN A CEMENT KILN AT SAN JUAN CEMENT

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INTRODUCTION

Some attractive alternatives to hazardous-waste incineration which make use of a waste's heat content are cofiring of hazardous wastes in high temperature industrial processes. Many such processes, which include cement and dolomite kilns, glass furnaces, steel furnaces, and some industrial boilers, provide conditions of temperature and residence time similar to those required for dedicated hazardous-waste incinerators. In addition to the savings derived from the heat value, the use of existing industrial processes requires less capital to process a given amount of hazardous waste.

In particular, cement kilns, because of large process capacities and energy use, appeared to be an excellent example of this concept. They typically operate at temperatures over 1,260°C (2,300°F), gas residence times are in excess of 1.5 seconds at or above this temperature, and the combustion zone is highly turbulent. The alkaline environment in a cement kiln absorbs acid gases such as HCl, and the need for exhaust gas scrubbing systems is eliminated.

Because of the need to gather more data on the cement kiln incineration of hazardous waste, Industrial Environmental Research Laboratory-Cincinnati conducted a comprehensive demonstration program at San Juan Cement in Dorado, Puerto Rico, from October 1981 until February 1982. The purpose of the demonstration program was to evaluate the ability of a cement kiln to destroy wastes, generate data for the purpose of formulating permitting criteria, and evaluation of the kiln's ability to remove the HCl combustion product. A sampling program was conducted during the burning of the hazardous waste. The primary goal of the program was to evaluate the effects of various waste parameters on the destruction efficiency of Principal Organic Hazardous Components (POHC's), and change in emissions of particulate matter, hydrocarbons, CO, SO_2, NO_x, and HCl. Secondary objectives were to detect and quantify the Products of Incomplete Combustion (PIC's), chlorinated dibenzofurans, chlorinated dibenzodioxins, trace metals and heavy organics.

A number of cement plants have been used to test cofiring of hazardous wastes, e.g., St. Lawrence Cement Company in Mississauga, Ontario in 1974-1976; Peerless Cement Company in Detroit, Michigan, in 1976; Stora Vika Cement Plant near Stockholm, Sweden, in 1978; and Marquette Cement in Oglesby, Illinois, in 1981. The data from these tests indicated that cement kilns, when properly operated, could destroy many of the organic chemical compounds in the wastes burned under the operating conditions of these tests. A need remained within EPA for criteria to use in evaluating whether or not to regulate cement plants which wish to burn wastes, particularly those which are highly chlorinated hydrocarbons.

The facility at San Juan Cement Company was chosen for the test due to its availability, the willingness of the company to cooperate with the Puerto Rican Environmental Quality Board (PRJCA) and U.S. EPA Region II in obtaining permits, and the suitability of the facilities for a test.

FACILITY AND PROCESS DESCRIPTION

San Juan Cement Company has operated a cement plant in Barrio Espinosa in Dorado, Puerto Rico, since 1970. The location of the plant is about 27 km west of San Juan. The San Juan Cement plant is dedicated to the manufacture of portland cement. Its annual production averages 4.082×10^8 kg (450,000 tons) per year and it employs 350 workers; it is the second largest cement plant in Puerto Rico.

The cement kiln is the heart of the cement process, as depicted in Figure 1. A cement kiln is a large steel horizontal tube with refractory linings. Such kilns may be up to 7.6 m in diameter and over 232 m long; at San Juan Cement, kiln #2 is 137 m (450 feet) long with an outer shell diameter of 3.05 m (10 ft) and 0.305 m (12 inch) thick walls. The kiln rotates slowly (75 rotations per hour) and has a gentle slope (0.3 m/10 m length) to allow material to pass through by gravity. Cement kilns are counter current; i.e., solid materials travel in one direction and hot gases plus dust emissions travel in the opposite direction. A slurry of 30-40% water (typically 35-39%) and finely crushed rock is fed into the kiln at the upper end. At the opposite end of the kiln is a powerful oil fire; at San Juan Cement kiln #2, No. 6 fuel oil is burned at about 1.51×10^{-3} m^3/s (24 gpm), a heat input of approximately 62×10^6 watts (212 million Btu/hr). As the raw material passes slowly through the kiln (1-4 hours), it first dries, then, at a temperature of 550°C (1,020°F), calcination starts (CO_2 is extracted from the calcium carbonate in the feed), and finally it approaches the hot burning zone of the kiln. In the burning zone, 1,500°C (2,700°F) temperatures calcine and fuse the raw materials creating a complex calcium silicate alumino-ferrite mineral substance called "clinker," which is discharged from the lower end of the kiln and cooled by large fans in the clinker cooler [1]. The clinker production rate at San Juan Cement ranged from 28-33 metric tons/hr (31-36 ton/hr). The addition of about 6% gypsum to milled clinker completes the process in the production of portland cement.

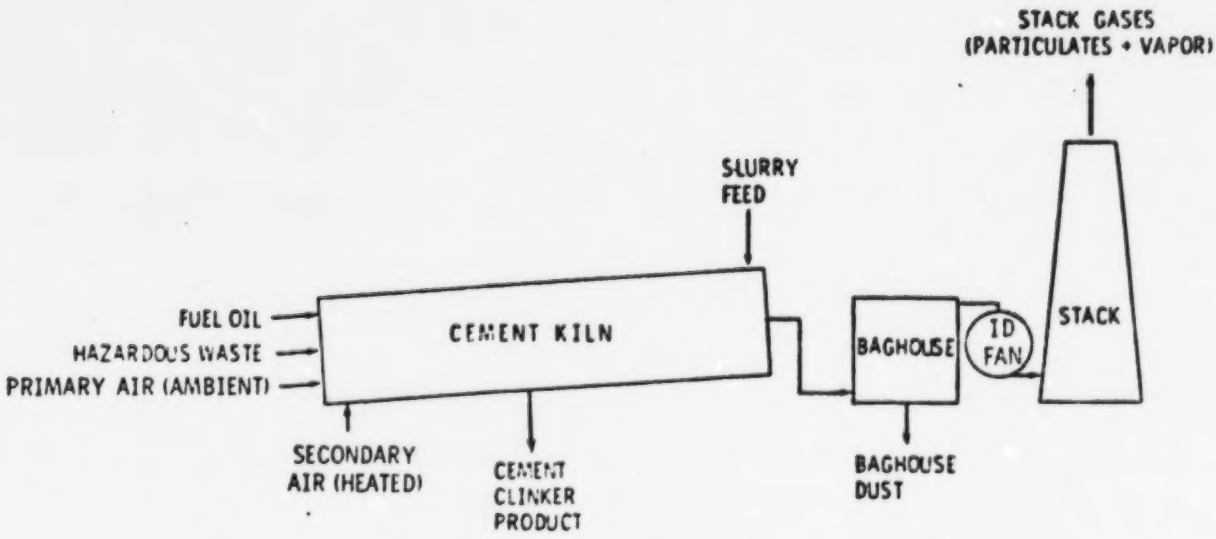

Figure 1. Schematic diagram of cement kiln burning hazardous waste.

Inputs

- fuel oil
- hazardous waste
- slurry feed

Outputs

- clinker product
- baghouse dust
- stack emissions, including
  - particulates
  - HCl vapor
  - unburned chlorinated hydrocarbons

Exhaust gases from kiln #2 pass through a baghouse type dust collector where entrained particulate matter is removed. The cleaned exhaust gases are then released to the atmosphere through a single stack. The baghouse employed at kiln #2 consists of 1,536 fabric filters, each 9.3 m in length. The efficiency of the baghouse in removing particulate matter from the gas stream was reported to be 99.8 percent. It was not an objective of this program to determine the baghouse collection efficiency.

EXPERIMENTAL DESIGN

The sampling and analytical program was designed to identify all major pollutants from the burning of the hazardous wastes available for this program and to quantify their respective emission rates, investigate the chlorine material balance of the cement process, determine burning rate limits as related to product acceptability and refractory lining integrity, and determine the destruction and removal efficiencies (DRE) of the principal organic hazardous constituents (POHCs) in the waste fuels. The POHCs chosen for this program were the three chlorinated compounds known to be present in the waste fuel mixture:

(1) Methylene chloride (dichloromethane), CH_2Cl_2
higher heating value (HHV) = 3058 Btu/lb

(2) Chloroform (trichloromethane), $CHCl_3$
HHV = 1349 Btu/lb

(3) Carbon tetrachloride (tetrachloromethane), CCl_4
HHV = 432 Btu/lb

Emission measurements included particulate matter, carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), nitrogen oxides (NO_x), hydrogen chloride (HCl), total gaseous hydrocarbons (THC), total chlorinated hydrocarbons, methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), trace metals in particulate matter, organics with special attention given to dioxins, and furans in the baghouse flyash. Chlorine content of the baghouse flyash and cement clinker was also monitored. The waste fuels and fuel oil used to fire the cement kiln were analyzed for principal organics, trace metals, ash, chlorine, nitrogen, and sulfur content.

Table 1 summarizes the test matrix of the demonstration program wherein the waste feed rate to the kiln and the chlorine content of the waste were varied. Table 2 summarizes the overall test program and shows each collection method and analytical method. A Quality Assurance Project Plan was prepared and reviewed prior to the program. A full description of the QA/QC results involving replicates, splits, blanks, spikes, and reference standards is provided in the report/final.

RESULTS AND DISCUSSION

A detailed summary of the waste fuel composition of each of the six waste batch shipments is given in Table 3. A seventh waste batch was burned and tested, which was a mixture of Batches 4 and 6.

TABLE 1. TEST MATRIX OF WASTE FEED RATE AND CHLORINE CONTENT

Approximate waste feed rate to kiln, m^3/s (gpm)	Percent chlorine in waste, wt %						
	6.5	10.1	18.7	21.4	22.9	32.0	35.1
8.39×10^{-5} (1.33)		x					
9.46×10^{-5} (1.50)	x		x				
1.10×10^{-4} (1.75)			x				x
1.26×10^{-4} (2.00)		x		x			
1.89×10^{-4} (3.00)						x	
2.21×10^{-4} (3.50)		x		x			x
2.71×10^{-4} (4.30)				x			
3.15×10^{-4} (5.00)					x	x	
3.47×10^{-4} (5.50)		x					
3.79×10^{-4} (6.00)		x					

x = Conditions tested.

TABLE 2. SAN JUAN CEMENT COMPANY WASTE FUEL DEMONSTRATION BURN SAMPLING AND ANALYTICAL PROGRAM

Parameter measured	Sampling method	Analytical method
Stack Samples		
Particulate matter	EPA Method 5	EPA Method 5
Metals on particulate	EPA Method 5	ICAP
Organics on particulate	EPA Method 5	Extractions and GC/MS for principal organics, dioxins, and furans
Opacity	EPA Method 9	EPA Method 9 (on site)
Sulfur dioxide	EPA Method 6	EPA Method 6
Nitrogen oxides	EPA Method 7	EPA Method 7
Carbon monoxide	EPA Method 10	NDIR continuous analyzer
CO_2 and O_2	Integrated bag sample	EPA Method 3 (on site)
Hydrogen chloride	Impinger train	Specific ion electrode
Total gaseous hydrocarbons	Direct to analyzer	Continuous FID
Total chlorinated hydrocarbons	Integrated bag samples	GC/EC (on site)
Three chlorinated species (POHCs)	Integrated bag samples	GC/EC (on site)
Organic compound speciation	SASS train	GC/MS
Ambient Air		
Particulate matter	High volume gas sampler	EPA-Appendix B FR 121:0105
Process Water		
Organics (3 species)	Integrated sample	EPA priority pollutant methodology, GC/MS
No. 6 Fuel Oil		
Btu content	Grab	ASTM D240-64
Chlorinated methanes	Grab	GC/EC
Sulfur content	Grab	ASTM D-3177
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
Waste fuel		
Btu content	Grab	ASTM D240-64
Moisture content	Grab	GC/MS
Total chlorine	Grab	ASTM D8081
Total nitrogen	Grab	Kjeldahl
Total sulfur	Grab	ASTM D129
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
PCBs and pesticides	Grab	GC/MS and GC/EC
Ash content	Grab	ASTM D482-IP4
Solid Waste (kiln dust)		
Principal organics	Grab	Extraction and GC/MS
Furans and dioxins		
Chlorine content	Grab	ASTM D-808
E.P toxicity	Grab	
Furans and dioxins		Extraction and GC/MS
Trace metals		ICAP

TABLE 3. SUMMMARY OF WASTE FUEL ANALYSES FOR CEMENTO SAN JUAN DEMONSTRATION BURN (volume basis)

Compound	Batch 1, vol %	Batch 2, vol %	Batch 3, vol %	Batch 4, vol %	Batch 5, vol %	Batch 6, vol %	Batch 4/6, vol %	Density, g/mL	TLV,[c] mg/m³
Water	<1.0	4.1	4.3	8.9	23.0	2.0	NA	1.000	-[d]
Methanol	10.4	7.1	13.9	6.2	10.9	ND[e]	NA	0.7914	260
Ethanol	0.8	3.2	8.6	4.7	16.8	5.6	NA	0.7983	1,900
Acetone	14.2	12.2	11.2	10.5	4.6	2.2	NA	0.7899	2,400
2-Propanol	4.7	5.2	5.3	4.5	3.1	1.6	NA	0.7855	500
Methylene chloride (POHC)	24.4	16.9	12.0	12.1	1.4	5.0	5.1	1.3266	360
Hexane isomers	3.9	3.2	1.8	1.5	ND	1.5	NA	0.6532	-[d]
3-Methylpentane	5.4	4.6	2.7	3.2	ND	3.6	NA	0.6645	-[d]
Hexane	19.8	17.3	7.2	8.5	5.9	15.7	NA	0.6603	1,800
Chloroform (POHC)	1.0	0.8	3.4	5.4	4.0	0.1	0.9	1.4832	50[f]
Ethyl acetate	4.0	14.0[b]	9.0	6.6	3.5	22.7	NA	0.9003	1,400
Methyl acetate	ND	NA	0.4	<1.0	ND	ND	NA	0.9330	610
Carbon tetrachloride (POHC)	0.8	0.6	1.4	10.2	7.8	0.01	1.5	1.5940	35[f]
Benzene	0.4	0.4	0.2	0.3	0.1	0.05	NA	0.8787	35[f]
Hexamethyl disiloxane	0.1	ND	ND	NA	NA	NA	NA	0.8923	-[d]
Toluene	0.2	0.1	0.02	<0.5	ND	ND	NA	0.8669	375
Acrylonitrile	ND	1.0	1.1	<0.7	1.0	ND	NA	0.8060	5[f]
Methyl ethyl ketone	NA	NA	0.08	1.1	NA	NA	NA	0.8054	590
C_8-benzene isomer	NA	NA	1.33	0.5	0.9	2.2	NA	0.90[e]	-[d]
C_8-benzene isomer	NA	NA	ND	NA	ND	23.8	NA	0.90[e]	-[d]
Sec-butyl ethylbenzene	NA	NA	1.23	1.7	NA	NA	NA	0.90[e]	-[d]
Xylene isomers	NA	NA	0.24	NA	NA	ND	NA	0.87[e]	435
Dimethylphenol isomer	NA	NA	0.04	NA	ND	ND	NA	0.90[e]	-[d]
1,1'-(1,2-ethanediol)bis-4-methoxybenzene	NA	NA	0.23	NA	NA	NA	NA	0.90[e]	-[d]
Unknowns	8.9	9.3	14.3	11.9	17.9	13.9	NA		
PCBs, ppm	<50	<100	<100	<100	<100	<100	<100		
Pesticides[g], ppm	<100	<100	<100	<100	<100	<100	<100		
Properties									
Btu content, Btu/lb	11,188	11,198	11,022	10,099	4,546	13,098	NA		
Specific gravity	NA	NA	0.9948	0.9885	1.0092	0.9163	0.9410		
Chlorine content, wt %	32.0	22.9	21.4	35.1	18.7	6.5	10.1		
Ash content, wt %	0.30	0.20	0.38	0.23	0.31	0.046	NA		

[a] ND = not detected, generally <0.1% by volume. Components were quantified in volume % because external standards were prepared on a volume basis.

[b] NA = not analyzed.

[c] Threshold limit value for workplace air.

[d] No TLV assigned to this compound or isomer.

[e] Estimated values.

[f] Suspected or known carcinogen.

[g] As per priority pollutant list.

A total of five comprehensive baseline tests (no waste fuel burned) were completed in order to determine the differences between when waste fuel was burned and when it was not burned. Four of the baseline testing days involved EPA Method 5 testing and the fifth test was a SASS run. The SASS was used to identify PICs and quantify dioxins and dibenzofurans.

When waste fuel was burned, ten comprehensive tests on seven different waste fuel batches were completed. These included SASS runs on waste batch numbers 3, 4, and 6; and EPA Method 5 runs on seven waste fuel burn tests. POHC testing and CO monitoring were conducted on fourteen additional tests.

Measurements of several conventional pollutants were made repeatedly during the program to determine the difference in emissions between baseline operation (no hazardous waste fed to the kiln) and waste fuel burns. Table 4 presents the comparisons for particulate, NO_x, SO_2, total hydrocarbon, and HCl emissions using the t-test to determine statistically significant difference.

TABLE 4. COMPARISON OF POLLUTANT LEVELS BETWEEN NORMAL OPERATION AND WASTE FUEL FIRING IN CEMENT KILN NO. 2, SAN JUAN CEMENT COMPANY

Pollutant	Mean loading		Statistical significance at 95% degree of certainty
	Baseline	Waste firing	
Particulate matter	93 ± 65 mg/m^3[a] (n=4)	99 ± 65 mg/m^3 (n=7)	No significant difference
NO_x	136 ± 83 ppm (n=4)	68 ± 23 ppm (n=9)	Significant difference
SO_2	279 ± 243 ppm (n=4)	450 ± 245 ppm (n=6)	Significant difference
Total hydrocarbons	8.3 ± 2.1 ppm (n=9)	12.7 ± 2.1 ppm (n=7)	Significant difference
HCl	0.82 mg/m^3 (n=2)	3.3 ± 1.7 mg/m^3 (n=9)	Significant difference

[a] 95% confidence level.

In each case, pollutant concentrations were used rather than emission rate because the volumetric flowrate varied as much as 30%, and hence added another variable to the statistical analysis.

High carbon monoxide emissions are an indicator of incomplete combustion in the cement kiln. When the kiln combustion was stable, CO emission levels stayed below 10 ppm. However, any process

fluctuation or change in kiln variables caused a momentary excursion in CO emissions to levels greater than 1,000 ppm (0.1%), even during baseline testing.

A commonly occuring effect due to waste fuel introduction to the kiln is shown in Figure 2, and illustrates the approximately one-hour transition period and effect on CO emissions when waste burning was initiated. From 0800 hours to 0905 hours, the kiln was not buring waste fuel and CO emission levels hover at 0-40 ppm, indicative of stable kiln operation. As the waste fuel was introduced the CO levels rose rapidly beyond 1,000 ppm for approximately 20 min and then returned to levels below 100 ppm as the kiln operators stabilized operation.

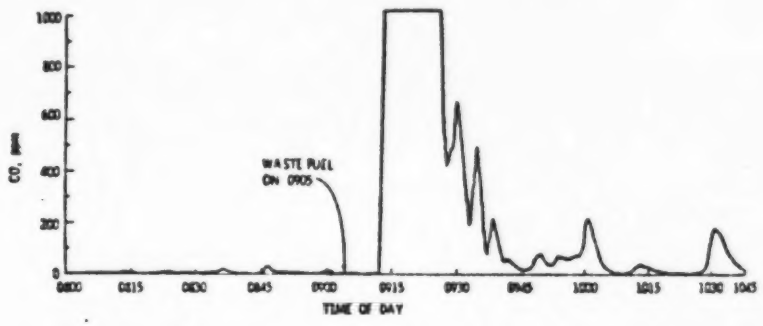

Figure 2. Illustration of waste fuel burn transition period effect on carbon monoxide emissions, Run W6-SASS-1, 28 January 1982, San Juan Cement Company.

POHC DESTRUCTION AND REMOVAL EFFICIENCY

The complex combustion chemistry for organic materials becomes perplexing when a broad range of organic compounds present in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO_2 in the combustion process, but trace amounts of organic chemicals survive the oxidation process and are only partially reacted. In addition, small amounts of other organic chemicals may be produced if proper conditions exist. Oxidative chemical principles would suggest that all organic compounds regardless of their origin would be converted to CO_2 and other primary products if a sufficiently high temperature is achieved in the presence of adequate oxygen for a time long enought for complete oxidation to occur. If the conditions of temperature, time, and oxygen are not met, the combustion of the organic material in the fuel, plus any new organic components formed in the combustion process, would be expected to be incomplete and some possibly detrimental compounds of concern may then appear in the effluents [2]. This demonstration program investigated the amount of destruction of the organic compounds in the waste (DRE of the POHCs) and the types of organic compounds formed (PICs).

Currently, cement kilns which burn hazardous wastes are not regulated under RCRA. However, kiln performance in destroying waste was compared to that required for hazardous waste incinerators.

Destruction and removal efficiency (DRE) for an incineration/air pollution control system is defined by the following equation:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} (100\%)$$

where DRE = destruction and removal efficiency, %
W_{in} = mass feed rate of the principal organic hazardous constituent(s) to the incinerator
W_{out} = mass emission rate of the principal organic hazardous constituent(s) to the atmosphere (as measured in the stack prior to discharge).

Within the family of chlorinated hydrocarbons, the monocarbon compounds are believed to be among the most difficult to thermally destroy. The carbon-chlorine bond is especially tenacious and, in general, the more C-Cl bonds present, the more difficult a compound will be to destroy. Accordingly, a monocarbon chlorine-containing molecule will tend to be harder to thermally destroy than a two carbon chlorine-containing molecule. The Gibbs free energy of formation values at 1600°C (2421°F) illustrate this, where the amount of energy required to form a molecule (conversely, the "difficulty" required to destroy) can be expressed as:

$$CCl_4 > CHCl_3 > CH_2Cl_2 > C_2H_3Cl_3$$

Concentrations of the POHCs were measured during baseline testing (days when no waste fuel was burned) in order to give background or normal concentrations of the POHCs in the exhaust gas. The average background level was then subtracted from the results obtained during a waste fuel burn to arrive at the contribution attributable to the waste burn.

The average DRE for each test run for the POHC's is presented in Table 5. Methylene chloride was destroyed to at least 99.0% efficiency, with the only exceptions being the two tests with waste batch #5 which contained only 1.4% methylene chloride. In general, the lower the mass feed rate of a POHC, the lower the DRE was.

Chloroform and carbon tetrachloride were more difficult to destroy than methylene chloride. Also, in most waste batches, methylene chloride was the most bountiful POHC in the waste. Waste batches #4 and #5 had the largest amounts of chloroform and carbon tetrachloride, and the best DRE results for carbon tetrachloride were

TABLE 5. DESTRUCTION AND REMOVAL EFFICIENCIES OF POHC's FOR DEMONSTRATION BURN TESTS AT SAN JUAN CEMENT COMPANY KILN #2

Run number	Methylene chloride	Chloroform	Carbon tetrachloride
W1-2[a]	>99.997	>99.842	99.309
W2-1[a]	99.995	>99.859	>99.996
W3-1	>99.991	99.887	91.043
W3-2	99.960	99.932	96.864
W3-3	99.659	>99.960	98.977
W4-1	98.237	98.592	97.732
W4-2	99.418	99.470	98.122
W4-3	99.461	99.283	99.142
W4-4	99.984	98.975	99.684
W4-5[c]	99.335	99.950	99.069
W5-1[c]	93.292	98.388	99.553
W5-2[c]	96.663	96[b]099	99[b]460
W6-1	99.223	-	-
W4/6-1[c]	99.760	95.617	94.129
W4/6-2[c]	99.668	92.171	99.325
W4/6-3[c]	99.564	98.703	94.512
W4/6-4[c]	99.133	>99.737	92.253
W4/6-5[c]	99.474	97.515	95.873

[a]Waste feed rate was estimated.

[b]Not present in waste fuel

[c]Stack gas volumetric flow rate of 1619 dscmpm used.

observed for the test runs on these two batches. Figure 3 illustrates the frequency of obtaining a certain "number of nines" of DRE for each of the POHC's in the demonstration program. In few instances was the desired 99.99% or even 99.9% DRE obtained for the chlorinated monocarbon compounds chosen as POHC's in this program.

In one instance, run number W6-1 for CCl_4, the W_{out} exceeded the W_{in}. The mass feed rate to the kiln was less than 0.11 kg/hr, and the higher mass emission rate observed suggests that CCl_4 is formed as a product of incomplete combustion from the combustion of methylene chloride and chloroform.

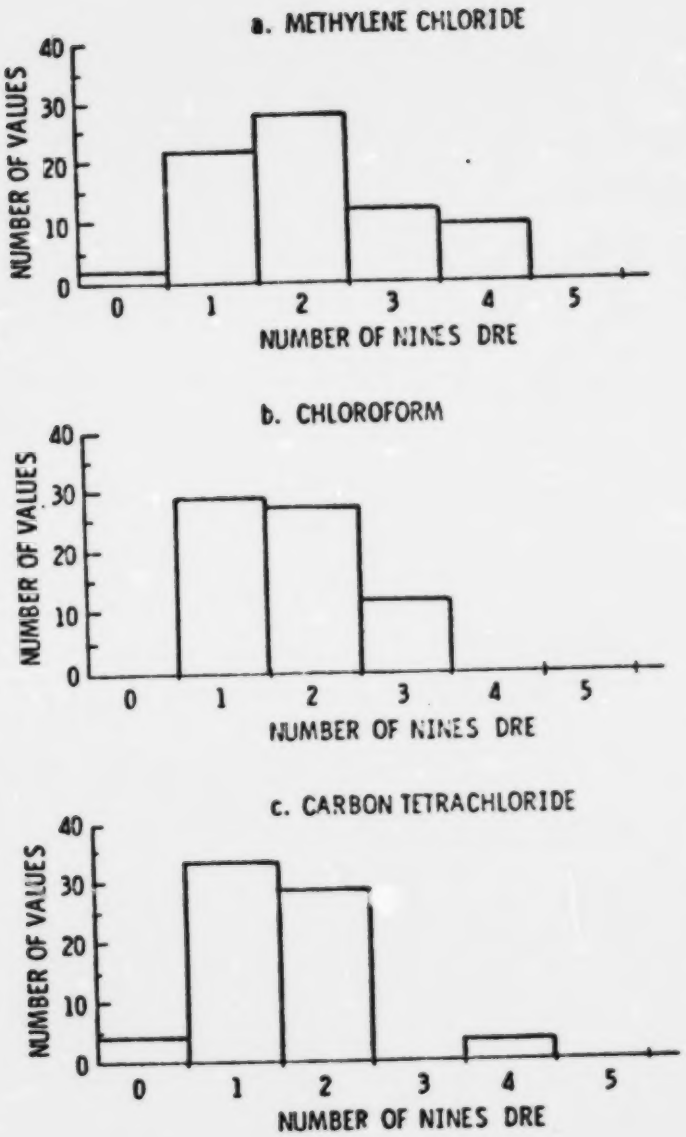

Figure 3. Distribution of DRE results for each POHC.

There are two probable reasons which can be used as explanations for the low DRE results obtained in the demonstration program: (1) lack of atomization of the waste fuel, and (2) difficulty of incinerability of highly chlorinated monocarbon compounds. The waste fuel injection had to match the fuel oil injection pattern in order to prevent flame impingement on the inner wall of the kiln and pre-ignition, or back-puffing, of the fuel oil stream. Therefore, methods to increase the waste fuel atomization were not attempted.

Other compounds were detected by the GC/EC during the analyses for the POHC's, which eluted at retention times of 0.51 min (CH_2Cl_2), 0.80 min ($CHCl_3$), and 1.01 min (CCl_4). The most commonly seen compound had a retention time of 0.57 to 0.61 min, which a post-test laboratory experiment with duplicate GC conditions tentatively identified as trichlorotrifluoroethane. This compound most probably was Freon 113 from the laboratory's air conditioner. Another compound which was seen in several instances eluted at about 1.1 min and was tentatively identified as trichloroethylene, a likely PIC from chloromethane combustion. 1,1,1-trichloroethane (1.54 min R.T.), tetrachloroethylene (1.68 min R.T.), acetone (2.11 min R.T.), acetonitrite (2.15 min R.T.), and acrylonitrile (2.16 min R.T.) were never detected by the in-field GC/EC analyses.

The SASS samples collected for chlorinated dioxins and chlorinated dibenzofurans were also analyzed for products of incomplete combustion. Four samples (one baseline and 3 waste burning) were analyzed for PIC's. The baseline sample was analyzed since the cement plant burns fuel oil as its primary energy source. During the program, fuel oil accounted for 87 to 100% of kiln's energy requirement. Products of incomplete fuel oil combustion need to be distinguishable from products of incomplete hazardous waste combustion - hence the baseline sample. Three SASS samples were collected during hazardous waste burning representing different feed compositions, feed rates and operating conditions. Specific tests results are shown in Table 5-5, which contains positive and tentative identification as well as mass emission rates.

The PIC's which were not detected during the baseline test and can be considered attributable to hazardous waste burning are:

- Trichloroethylene (100-100,000 mg/hr)
- Phenol (2.4-11.0 mg/hr)
- C_2-naphthalene isomers (10-50 mg/hr)
- C_3-naphthalene isomers (14-46 mg/hr)

DIOXIN AND DIBENZOFURAN RESULTS

One of the objectives of the program was to determine if polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were emitted as products of incomplete combusion while

hazardous waste was being fired to the kiln. Cholorinated dioxins and dibenzofurans are believed to be among the most toxic substances to humans. EPA officials required that during the demonstration program extensive sampling and analysis be conducted for these compounds. During the course of the program, a total of 28 different samples were collected for analyses as shown below.

- 4 SASS train samples (particulates and vapors in stack gas);
- 5 EPA Method 5 samples (particulates in stack gas);
- 11 baghouse dust samples (plant solid waste);
- 8 RCRA extracts of baghouse dust samples (plant solid waste).

Eight samples were taken during baseline (nonburning) conditions and 20 samples were taken during hazardous waste burning operations. The SASS train samples resulted in three sections for analysis: 1) methylene chloride rinses of the sampling probe, teflon line, filter holder, and organic module, 2) combined filter and XAD-2 absorbent resin, and 3) the condensate water removed from the organic module during sampling.

The baseline (no waste fired) SASS run (BW-SASS) showed some positive, detectable values of hexachloro- and heptachlorodibenzofuran in the absorbent resin extract, although none could be detected in the other portions of the train. This caused the reported values to be less than the average detection limit for the entire train, which was 3.4 ng/m^3. It is noteworthy that no PCDD's or PCDF's were detected in any waste burning SASS samples at a detection limit ranging from 1.6 ng/m^3 for tetrachloro-isomers to 4.9 ng/m^3 for octachloro-isomers.

In the analyses of the particulate catch from EPA Method 5 runs, no detectable quantities of PCDD's were found in any of the particulate samples. In only one sample, run W3-3, 11.0 ng/m^3 of pentachloro-PCDF, 26 ng/m^3 of hexachloro-PCDF, and 8 ng/m^3 of heptachloro-PCDF isomer were found. These detectable emissions occurred when the kiln was fed 2.75×10^{-4} m^3/s (4.35 gpm) of waste which contained 21.4% chlorine. This corresponds to a chlorine input of 3.5% by weight of total fuel input (fuel oil plus hazardous waste) which results in the production of off-spec cement clinker and a potentially kiln-damaging condition. Excessive chlorine in the clinker will lengthen cement set time and reduce strength. The Chlorine Material Balance section describes how this is an operating condition which is intolerable for the cement plant. Thus, the generation of detectable quantities of PCDF's occurred only when operating an "upset" or "out-of-control" kiln. Under other conditions the cement process did not emit PCDF's, and did not emit PCDD's under any waste buring conditions. This lack of detectable quantities of PCDD and PCDF is an expected result because the waste fuel contains no polychlorophenolate percursors, the combustion temperatures were typically well above 1000°C, and a supplemental fuel was used to burn the wastes [2].

CHLORINE MATERIAL BALANCE

The combustion of chlorinated hazardous wastes as auxiliary fuel in cement kilns results in the generation of hydrogen chloride (HCl) in the kiln. Hydrogen chloride can be absorbed by the clinker product, cement kiln lining, baghouse dust or emitted as part of the particulate. Unabsorbed HCl will be emitted from the stack as will the unburned chlorinated hydrocarbons. HCl is formed rather than chlorine gas (Cl_2) because the conversion of chlorine gas to hydrogen chloride is favored by high temperatures and high water content in the combustion gas. Typically, the bruning zone temperature in a cement kiln is 1425°C (2600°F) with the moisture content equal to about 10-15%. Additional moisture is added to the combustion gases in wet process cement kilns in the slurry drying zone of the kiln. Equilibrium calculations show that 99.987% of the chlorine in the combustion gases will be present as HCl; only 0.013% of the chlorine will be present as chlorine gas. The HCl is rapidly absorbed by alkaline calcium, sodium, and potassium compounds present in the clinker and dust to form sodium, potassium, and calcium chlorides.

In addition to calcium, the major element of the cement-making process, sodium and potassium are important impurities in the raw feed material. They are undesirable in the clinker and are normally removed by the addition of chloride to the kiln --either in the form of calcium chloride or as HCl. The resultant NaCl and KCl volatilize at the temperature of the kiln, condense as a particulate in the cooler end of the kiln, and are removed by the air pollution control device. The amount of chloride that a given kiln can handle is limited by the sodium and potassium content of its feed. If excessive chlorides are added to the system, these salts can form a clinker ring in the kiln and possibly damage the refractory lining [3].

The distribution, or fate, of the chlorine (as chloride) was studied in seven tests by measuring the chlorine-chloride content of the input and output streams of the kiln. The material balance closures for chlorine ranged from 83% to 104% with an average closure of 92%.

It was found that at San Juan Cement, about 82% of the chlorine fed to the cement kiln will appear in the clinker product. The amount of chlorine in the clinker is presumed to be dependent, primarily, upon feed alkalinity, and will vary from cement plant to cement plant. Other cement plants with different slurry feed compostion and alkalinity will realize different results, e.g., up to 92% of the chlorine was retained in the clinker at St. Lawrence Cement in Missisauga, Ontario during those tests.

Normally, the potassium contained in the slurry feed leaves the kiln as potassium sulfate and potassium oxide and is collected in the baghouse. Presumably, HCl reacts with K_2SO_4 to form KCl salt which is trapped in the clinker. The kiln operates above the dew point for H_2SO_4 (~160°C) and H_2SO_4 not absorbed by dust will leave as a vapor increasing SO_x emissions. Earlier it was shown that there is a "statistically significant change" in SO_x emissions when buring hazardous waste. The average SO_x emission rates may indeed by higher due to the chemistry of the inorganic elements in the kiln; i.e., the chloride acid gas is trapped (scrubbed) preferentially over the sulfate acid gas.

The amount of chlorine appearing in the stack emissions as unburned chlorinated hydrocarbons ranged from 0.076 to 4.3% which represented appropriate overall destruction and removal efficiencies (DRE) of 99.924% down to 95.7% on a total chlorinated hydrocarbons feed basis. The tests showed lower DRE's when burning higher levels of carbon tetrachloride. The total absorption of HCl by the cement kiln process averaged 99.7% in seven tests.

The amount of chlorine appearing in the baghouse dust varies from 5% to 26% of the total chlorine feed. The amount of chlorine appearing in the baghouse dust is influenced by the concentration of chlorine in total fuel (fuel oil plus hazardous waste).

Figure 4 shows the dramtic increase in chlorine concentration in baghouse dust when chlorine comprises 3% by weight or more of the total fuel. The plant always went into an upset condition about 90 minutes after the start of a trial burn which had 3% or more of chlorine in the total fuel. Some key observations based on the experience of saturating this kiln with chlorine are:

- The cement kiln will remain in a stable and controlled operating condition when the chlorine content of the total fuel (fuel oil plus hazardous waste) is 3% (by weight) or less. When chlorine content exceeds 3%, the kiln becomes operationally unstable about 90 minutes after the start of burning more than 3% chlorine in the total fuel. The instability takes several forms. The burning zone temperature drops from 1430°C (2600°F) to <615°C (1500°F) 90 minutes into the burn. The kiln starts a rapid loss of refractory lining (coating) to cement clinker product. A clinker ring forms in the burning zone. Hydrocarbon emissions increase (about fourfold) in the stack.

- Recovery from this upset condition is achieved by shutting off the hazardous waste while maintaining a constant heat balance. Remarkably, the kiln recovers in 12 to 15 minutes if the waste is shut off as soon as kiln goes into an upset condition. Continued operation during an upset would destroy the kiln. It is presumed that the excess chlorine is absorbed

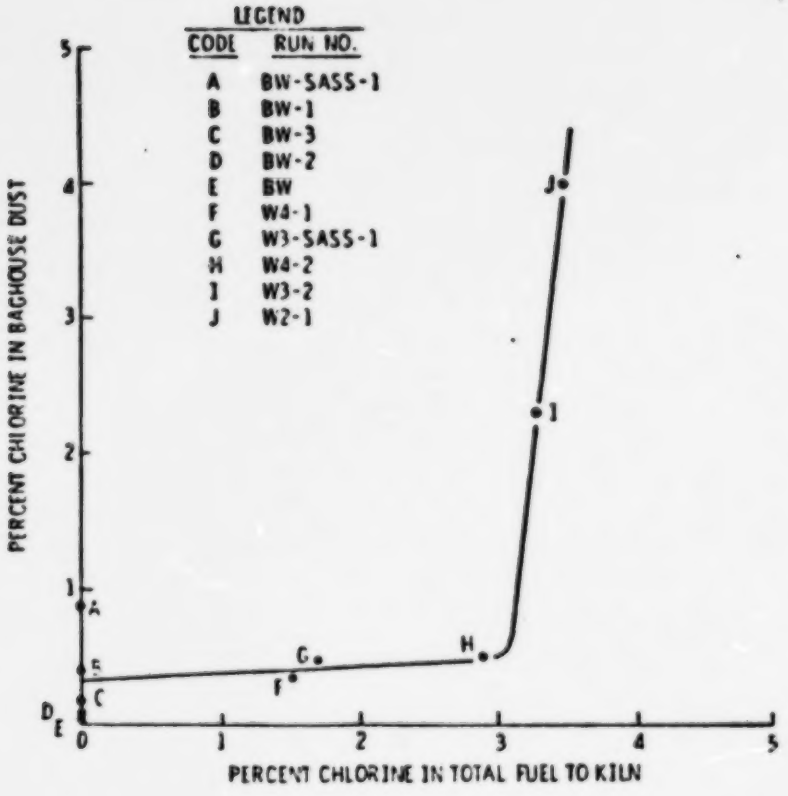

Figure 4. Effect of chlorine concentration in total fuel (fuel oil + hazardous waste) on chlorine content of baghouse dust at San Juan Cement.

in the lining and reduces its slagging temperature to below 815°C (1500°F). When the lining starts to slag, all heat goes to melt the lining, not to making cement. It is presumed that the kiln recovers in about 15 minutes because it takes the burning zone about 15 minutes to purge itself of slagged lining. Recovery is as dramatic as is the upset.

- Even though the cement kiln remains stable up to about 3% chlorine in the total fuel, the product quality becomes unacceptable when the chlorine content exceeds 1% of the total fuel at San Juan Cement.

- Clinker rings can be formed by either temperature excursions in the burning zone when not burning hazardous waste or by excessive chlorine additions to the kiln. Operators at San Juan Cement were successful at breaking clinker rings simultaneous with burning chlorinated hazardous waste. It was not required to cease hazardous waste buring to break a clinker ring.

Incineration of hazardous wastes in cement kilns also demonstrated a time delay in release of chlorine from the kiln. The onset of unstable kiln operations some 90 minutes after excess quantities of chlorine are added to the kiln was just described. Figure 5 shows dynamic behavior of chlorine releases from the cement kiln compared to a constant, short duration, and a moderate, but still excessive, chlorine feed rate to the cement kiln where it can be seen that it actually takes about three hours for the kiln to completely purge itself of the added chlorine.

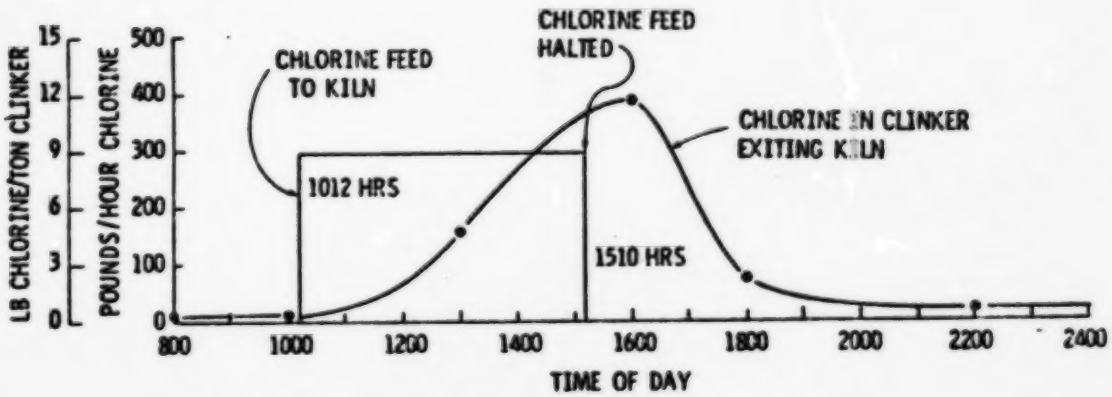

Figure 5. Fate of added chlorine in cement clinker producton.

CONCLUSIONS

Some of the results observed in this demonstration program were contradictory to results from other cement kiln incineration tests, e.g., lower DRE's, no change in particulate emissions, and significant changes in SO_2 and NO_x emissions. The conclusions presented below apply only to this particular kiln and the results from this demonstration program.

1. The inability of this kiln to consistently achieve 99.99% DRE (a value which hazardous waste incinerators must demonstrate) of the POHC's is attributed to unatomized waste introduction to the kiln flame and the difficult incinerability of the POHC's. These compounds (CH_2Cl_2, $CHCl_3$, and CCl_4) are occasionally employed as fire retardants because of their ability to remove hydrogen atoms from the free-radical branching combustion reactions to form HCl. Combustion of chlorinated species containing less chlorine may have resulted in higher DRE's.

2. Chlorinated dioxins and chlorinated dibenzofurans are not produced at detectable levels (1.6 ng/m^3) when a cement kiln firing chlorinated wastes is operating normally.

3. Cement kilns will absorb over 99% (about 99.7%) of the HCl formed during the combustion of chlorinated hazardous wastes. This absorption is partitioned between the clinker and baghouse dust.

4. At San Juan Cement, approximately 82% of the chlorine fed to the cement kiln appears in the clinker. This limits the chlorine content of total fuel to less than 1%. This may vary at different cement plants since quarry alkalinity (ability to absorb chlorine) varies at each cement plant.

5. Achievable fuel savings are a function of the chlorine content of the waste and each plant's ability to absorb chlorine. At San Juan Cement, a hazardous waste containing less than 5% will result in at least a 20% savings in fuel costs. Higher fuel savings may be possible for higher chlorine contents at other plants.

6. Production of saleable cement product is possible when burning chlorinated hazardous wastes provided the plant's chlorine absorbability limit is not exceeded.

7. Atomization of the waste fuel would be desirable, if a flame configuration can be obtained which does not alter the primary fuel flame configuration.

8. High feed line pressure [1,380-2,070 kPa (200-300 psig)] is not required for waste injection to the kiln. This pressure requirement may change depending on the type of atomizing nozzle used.

9. There is no significant change in particulate emissions due to burning chlorinated hazardous wastes. This result was observed on a cement kiln equipped with a fabric filter air pollution control system. A cement kiln with an electrostatic precipitator may not achieve similar results due to a change in dust resistivity.

10. Emissions of sulfur dioxide, total hydrocarbons, and hydrogen chloride increased significantly when waste was burned. A cement kiln with a higher alkalinity feed than San Juan Cement may not have an increase in SO_2 emissions.

11. Emissions of nitrogen oxides decreased significantly when waste was burned.

12. There is no change in particulate ambient air quality due to hazardous waste combustion in cement kilns.

13. The solid waste (baghouse dust) generated by hazardous waste burning and its RCRA extract (leachate) are suitable for landfilling.

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